Deposition Process of Ni on Si(100) Surface in Aqueous Alkaline Solution

Daisuke Niwa[1], Nao Takano[2], Takayuki Homma[1], Tetsuya Osaka[1,2]

[1] Dept. of Applied Chemistry ;
[2] Kagami Memorial Lab. for Mat. Sci. and Tech.,
Waseda University,
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Metallization onto patterned surface of silicon wafer is one of the important processes for semiconductor device and MEMS manufacturing. We have developed the metallization process using electrochemical method, especially focusing upon electroless Ni deposition on Si(100) wafer surface in aqueous alkaline solution [1-2]. In our previous work, it was found that the Ni could be deposited on Si(100) wafer immersed in the pH-adjusted $NiSO_4$ solution without containing any reducing agent such as NaH_2PO_2. It was suggested that the Ni deposition for this process was accompanied by the formation of silicon oxide, nevertheless, the details has not been clarified yet.

In the present work, deposition mechanism of Ni on Si(100) surface in aqueous alkaline solution is investigated in detail by using electrochemical analyses and *in-situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR FTIR).

N-type Si(100) wafers (8-12 Ω cm) were used for the present work. The wafers were treated with SPM (96 % H_2SO_4 : 30 % H_2O_2 = 4 : 1) at 80 °C followed by rinsing with 18 MΩ cm deionized (DI) water. The wafers were immersed in 1.0 % HF for 30 sec to prepare clean, hydrogen terminated surface. Then the wafer surface was mildly oxidized with HPM (36 % HCl : 30 % H_2O_2 : H_2O = 1 : 1 : 5) at 80 °C followed by rinsing with DI water, and was subsequently immersed into aqueous alkaline solution containing Ni [0.1 M $NiSO_4$ + 0.3 M $(NH_4)_2SO_4$ aqueous solution] at pH 9.0 and 80 °C. The specimens were observed using a scanning electron microscope (SEM). Amount of the Ni deposition was measured using an inductively coupled Ar plasma spectrophotometer (ICP). Electrochemical measurements of the wafers immersed into aqueous alkaline solution were carried out using an Ag/AgCl reference electrode. Chemical structure of the wafer surface in aqueous alkaline solution was monitored using *in-situ* ATR FTIR measurement.

Figure 1 shows electrochemical open circuit potential (OCP) profile and amount of Ni deposition at each immersing time. The deposition reaction is initiated as OCP shift toward negative direction around 10-20 sec (Fig. 1 (1)), and no increase in the amount of Ni deposition is observed as the OCP shifts positively after 160 sec (Fig. 1 (2)). The potential at 160 sec (-0.70 V vs. Ag/AgCl) corresponds to a redox potential in this measurement condition, indicating that the deposition reaction is self-ceased.

In order to clarify the origin of OCP shifts at (1) and (2), the OCP of the wafer in the solution excluding Ni ion was also measured (Fig. 2). Similar potential shift to that shown in Fig. 1 is confirmed, indicating that the deposition reaction mainly affects with an anodic reaction of Si. Next, the change in chemical structure of the wafer surface in the solution excluding Ni ion was investigated by the *in-situ* ATR FTIR measurement. Based upon these results, deposition process was discussed. A very thin layer of silicon oxide (ca.0.6 nm) on the wafer surface by the HPM was dissolved by the aqueous alkaline solution, and subsequently formed a sub-oxide rich surface as the OCP shifted negatively around the region (1). The surface consists of sub-oxide, Si-Hx and Si-OH bond, which were also active for the anodic reaction. Such a surface has been formed during the reaction phases. Then, chemical structure of Si wafer surface was changed drastically as the OCP shifts positively at the region (2) where the deposition reaction was stopped.

From these results, it was considered that the sub-oxide sites were active for the deposition reaction, and the Ni deposition spontaneously proceeded by the oxidation of sub-oxide bonds.

References

[1] N. Takano, N. Hosoda, T. Yamada, T. Osaka, *J. Electrochem. Soc.* **146** 1407 (1999).
[2] N. Takano, D. Niwa, T. Yamada, T. Osaka, *Electrochim. Acta* **45** 3263 (2000).

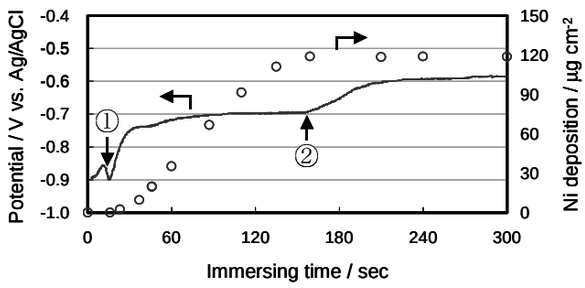

Figure 1 OCP curve and amount of Ni deposition of the wafer immersed in aqueous alkaline solution (pH 9.0 80 °C).

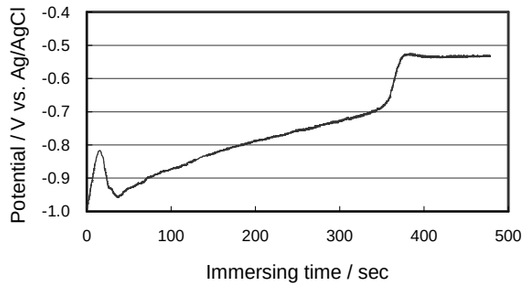

Figure 2 OCP curve of the wafer immersed in aqueous alkaline solution excluding Ni ion (pH 9.0 80 °C).